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13. ABSTRACT *(Maximum 200 Words)*

The research described in this Final Report was directed at studying the dynamics of vibrationally excited molecules, which are important in many energetic environments. The first goal was assembly of an ultrafast laser system producing 1-mJ, 100-fs pulses of 800-nm light, and implementing non-linear processes for converting those pulses to infrared and ultraviolet light. This system permitted the a direct measurement of the time for intramolecular vibrational energy flow in nitric acid ($HONO_2$) initially prepared with two-quanta of O-H bond stretching excitation.

The measurements showed that energy flowed out of that initially excited vibration in 12 ps, a time consistent with a coupling matrix element of about 0.08 cm^{-1}. This result on an isolated molecule sets the stage for the a similar measurement in a liquid.

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Final Report

Air Force Office of Scientific Research

Intramolecular and Intermolecular Energy Transfer
in
Highly Vibrationally Excited Molecules

Grant No.   F49620-95-1-0009

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Objectives

The goal of this research was to study the dynamics of highly vibrationally excited molecules, which are important in many high energy environments. With the help of a DURIP grant (F49620-95-1-0068), we carried the work in an exciting new directions with the goal of probing and controlling energy transfer processes, reactions, and photodissociation of highly vibrationally excited molecules in gases and *in liquids.*

Accomplishments

Our goals period of AFOSR support were to construct an apparatus for time-resolved photodissociation and energy transfer experiments in liquids, to make a first measurement on an isolated molecule, and to transfer that measurement into a liquid to discover the influence of the solvent on the relaxation. We developed an apparatus that performs well, directly measured the time of intramolecular energy flow in isolated nitric acid, and made our first measurements of photolysis in a liquid.

Ultrafast Laser System

Our approach requires tunable pulses of light that last about 100 fs and range from near ultraviolet to infrared wavelengths. A regeneratively amplified Ti:sapphire laser system that produces 80-fs duration pulses of 800-nm light at a repetition rate of 1 kHz is the starting point of the light generation. The 1 mJ of 800-nm light from this system (Clark MXR, CPA 1000) is the origin of other wavelengths that we create by nonlinear frequency conversion in an optical parametric amplifier (OPA), by frequency doubling and mixing in nonlinear crystals, and by continuum generation. We have installed the laser in a remodeled laboratory, built stabilization and diagnostic hardware (including a frequency resolved optical gating device), constructed and characterized a continuum seeded OPA, and assembled the requisite detection electronics and computers.

The Ti:sapphire oscillator produces a 100-MHz train of 100-fs pulses that a grating pulse stretcher lengthens to about 200 ps and injects into a Ti:sapphire regenerative amplifier pumped by a Nd:YAG laser. Pulses emerge from the regenerative amplifier at the 1-kHz repetition rate of its pump laser, and a grating compressor shortens the amplified, 1-mJ pulses to 70 fs duration. Optical parametric amplification of a portion of a single filament, white light continuum in a BBO crystal gives light in the range of 1.1 μm to 2.7 μm with a bandwidth of about 280 cm^{-1}. The phase matching angle of the crystal determines the wavelength of the amplified light. Double passing the signal beam from the OPA through the crystal produces about 100 μJ of radiation at 1.2 μm. Frequency doubling 1.2-μm light from the OPA in a BBO crystal yields 30 μJ of 600-nm light, which another step of frequency doubling converts to 10 μJ of 300-nm light. Thus, the combination of the OPA and frequency doubling allows us to cover a wide range of wavelengths with short pulses and good energy.

Intramolecular Energy Flow in an Isolated Molecule

Our first measurement illustrates the capability of the apparatus, produces data that are interesting in their own right, and provides the reference point for our new measurements in liquids. We have used the time resolution of our apparatus to monitor *directly* the flow of energy out of one bond in a vibrationally excited molecule. Our plan is to compare this directly determined intramolecular vibrational energy redistribution (IVR) time in an isolated molecule to the results of a similar measurement in solution.

Most work on the redistribution of vibrational energy has used frequency domain techniques to extract couplings between bright and dark zero-order states from high resolution spectra. From the analysis of such spectra, one can predict the time evolution of an initially localized state *if it were to be prepared*. There is less work on IVR in the time domain. Typically in time-domain experiments, a short laser pulse prepares a vibrationally excited state in the first electronically excited state S_1 through an electronic transition to a Franck-Condon bright state, and a second short pulse probes the IVR dynamics by fluorescence depletion, pulsed field ionization, or other spectroscopic techniques. We have extended these approaches by developing time-resolved vibrationally mediated photodissociation. We excite an initial localized vibration in the ground electronic state with one short laser pulse and monitor its relaxation by photodissociating the vibrationally excited molecule with a second short laser pulse.

Vibrationally mediated photodissociation is a double resonance technique: one laser pulse prepares a vibrationally excited molecule in its electronic ground state, and a second laser pulse, tuned to an electronic transition, photodissociates the molecule.In the ideal vibrationally mediated photodissociation experiment illustrated in Figure 1, the photodissociation laser pulse has too little energy to dissociate molecules with no initial vibrational excitation. However, since the excited state surface is repulsive and its potential energy decreases along the dissociation coordinate, the energy difference between the electronic ground state and the excited state decreases along this coordinate. Therefore, a less energetic photolysis photon can transfer vibrationally excited molecules that are elongated along the dissociation coordinate to the excited state surface. Even in less than ideal vibrationally mediated photodissociation experiments, vibrational excitation produces a substantial increase in dissociation yield. The key to using vibrationally mediated photodissociation to follow vibrational energy flow is to prepare a *non-stationary* vibrational state that the photolysis laser cannot dissociate and monitor the flow of energy out of that state into other states that the photolysis photon can dissociate.

The schematic potential energy surface in Figure 1 illustrates our time resolved measurement on nitric acid ($HONO_2$). Initially a 100-fs pulse of 1.44-μm light from the OPA excites two quanta of O-H stretching vibration, approaching the conceptual ideal of "plucking" a single bond. Another ultrashort pulse of 266-nm light photodissociates those molecules in which energy has migrated out of the O-H stretching vibration into other vibrations that promote the photodissociation. Because photodissociation of nitric acid yields, in part, electronically excited NO_2, we can follow the flow of energy out of the O-H stretch by observing emission from the electronically excited

NO$_2$ in the region of 480 to 580 nm as a function of the time, Δt, between the vibrational excitation pulse and the photolysis pulse.

Figure 1
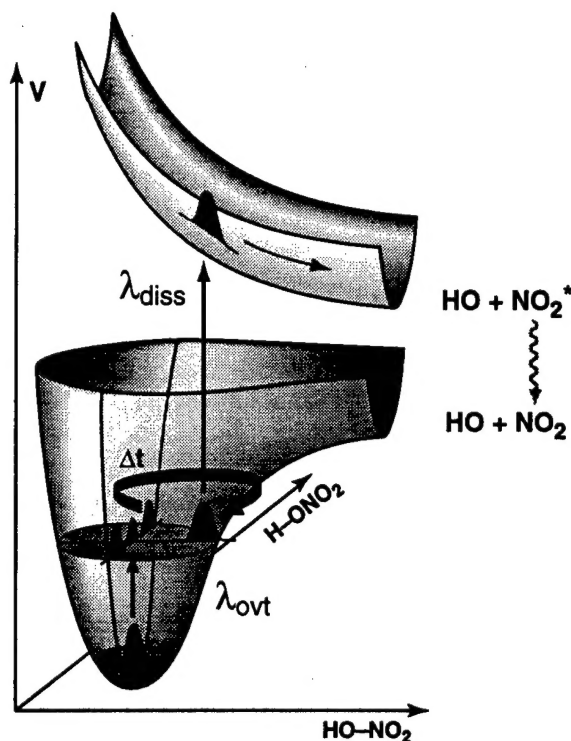
The circles in Figure 2 are the fluorescence signal from the NO$_2$ product of the vibrationally mediated photodissociation of a 250 mTorr, room temperature sample of HONO$_2$. (Beyond the 80 ps shown in the figure, there is no statistically significant change in the signal level out to 1 ns.) The solid line through the data is a single exponential rise with a time constant of $\tau = 12$ ps. *The measurement shows that energy flows out of the O-H stretching vibration in nitric acid in about 12 ps, corresponding to approximately 1200 vibrations of the O-H bond.* The spectra in Figure 3 identify the initial excitation. The vibrational overtone spectrum of nitric acid, taken by monitoring the photoacoustic signal from excitation of a sample with the 100-fs pulses, and the vibrational action spectrum, obtained by observing the NO$_2$ fluorescence signal with the delay between the lasers fixed at $\Delta t = 50$ ps, are identical as a function of the wavelength of the infrared light from the OPA.
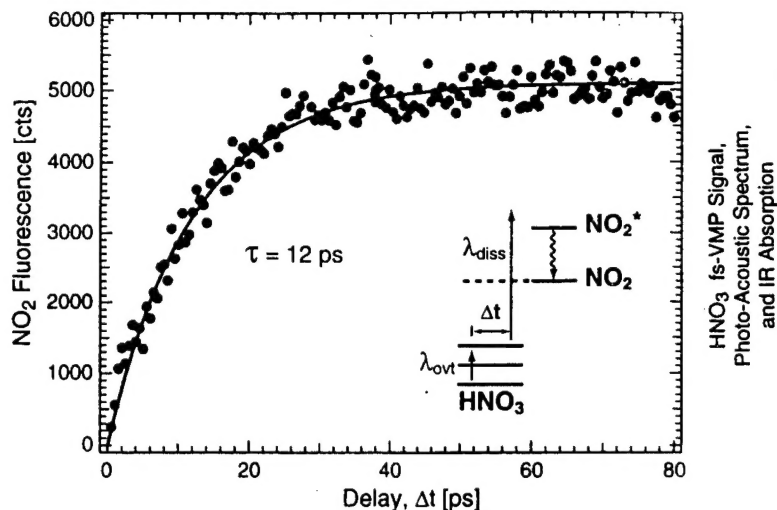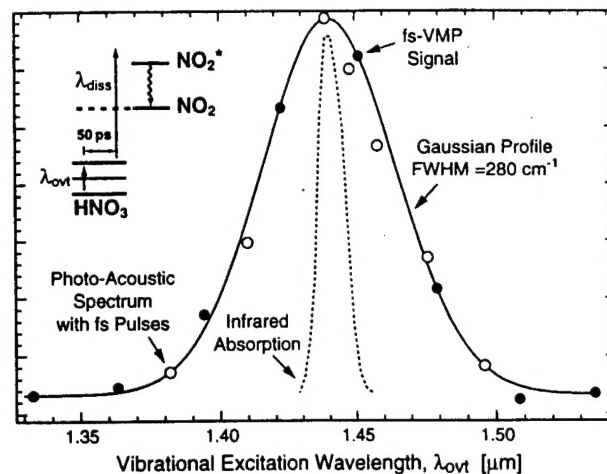
Figure 2

Figure 3

A simple estimate using the calculated state density (ρ =10 states/cm^{-1}) and the measured relaxation time (τ =12 ps) in Fermi's Golden rule, $\tau^{-1} = 4\pi^2 c |V|^2$, yields a coupling matrix element of $|V|$=0.08 cm^{-1}, a value consistent with, but lying on the high end of, those generally found for non-specific vibrational couplings. The measurement establishes the IVR time in the isolated molecule at 7000 cm^{-1} of internal energy and suggests that energy transfer among essentially all of the isoenergetic states in this five-atomic molecule is complete in tens of ps.

Intramolecular Energy Flow in a Solute Molecule

The measurement on gas phase nitric acid demonstrates ultrafast time-resolved vibrationally mediated photodissociation for the first time *and* provides the essential point of comparison with relaxation in solution. We are now transferring our measurement of the intramolecular energy redistribution time for nitric acid to a chloroform solution. A 100-μm thick sample of a dilute solution of HONO$_2$ in CHCℓ_3 flows through quartz cell through which the 1.44-μm vibrational overtone excitation light from the OPA and the 266-nm photolysis light propagate. Because the solvent quenches emission from the electronically excited state of NO$_2$ too quickly for fluorescence to serve as a detection technique, we probe the NO$_2$ product by electronic absorption around wavelengths of 400 nm. We frequency double a small portion of the 800-nm light from the Ti:sapphire laser and propagate it through the sample after a time delay of about 1 ns. As in the gas phase experiment, delaying the photolysis pulse relative to the vibrational overtone excitation pulse reveals the time for intramolecular energy transfer.
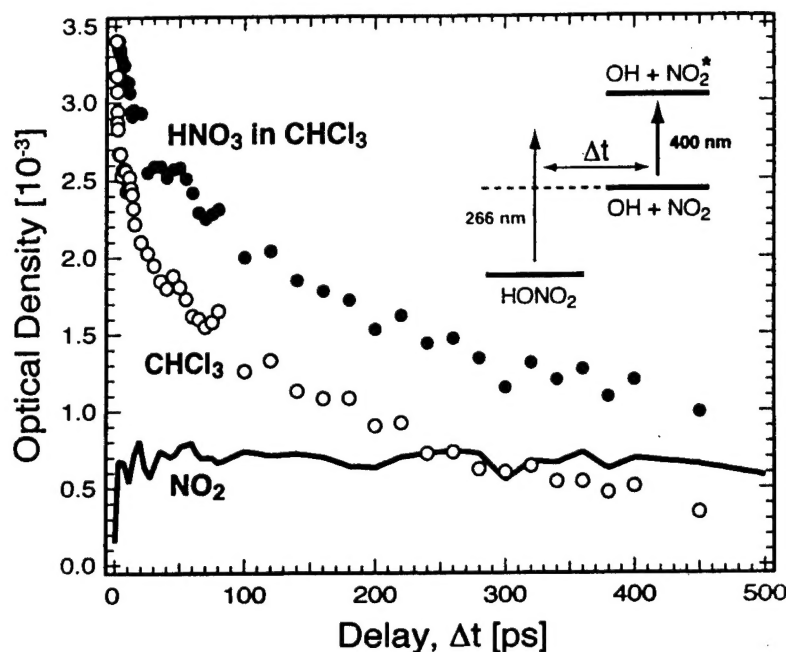
Figure 4

The first step in our experiments in liquids has been to photolyze a nitric acid solution and detect the resulting NO_2 product. Figure 4 shows the absorption of pure $CHC\ell_3$ and that of a 2% solution of $HONO_2$ in $CHC\ell_3$ as a function of the time between the initial 266-nm pulse and the subsequent 400-nm probe pulse. (The complex evolution of the signal as a function of the delay time, even in neat $CHC\ell_3$, is characteristic of nonlinear and multiphoton processes in liquids, a complication that we will in general avoid by fixing the delay between the photolysis and probe pulses at times larger than the transient artifact.) The increased absorption in the mixture, which appears as a displacement between the two curves, comes from NO_2 formed in the 266-nm photolysis of nitric acid. The difference in the signals (heavy solid line) shows that the NO_2 product appears in less that 500 fs and remains constant for hundreds of ps afterwards. Our calculations, based on the relative amounts of 266-nm photolysis background and vibrationally mediated signal in the gas phase experiment, predict a change in optical density of at least several times 10^{-4} as a result of the vibrationally mediated photodissociation, and the data in the figure clearly show that we can detect changes of that size. The photolysis of nitric acid in solution paves the way for the addition of the vibrational overtone excitation pulse and first observation of time-resolved vibrationally mediated photodissociation in solution. That result takes us directly to the determination of the IVR lifetime in solution.

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Publications

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